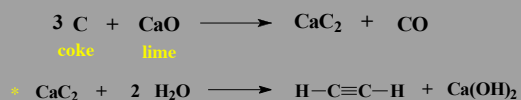


Synthesis of Acetylene

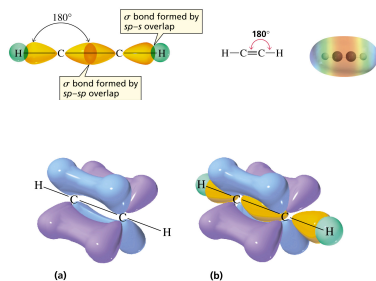
Heating coke with lime in an electric furnace to forms calcium carbide.

Then drip water on the calcium carbide.



**This reaction was used to produce light for miners' lamps and for the stage.*

The Structure of Alkynes



A triple bond is composed of a σ bond and two π bonds

Acidity of Acetylene and Terminal Alkynes



Acidity of Hydrocarbons

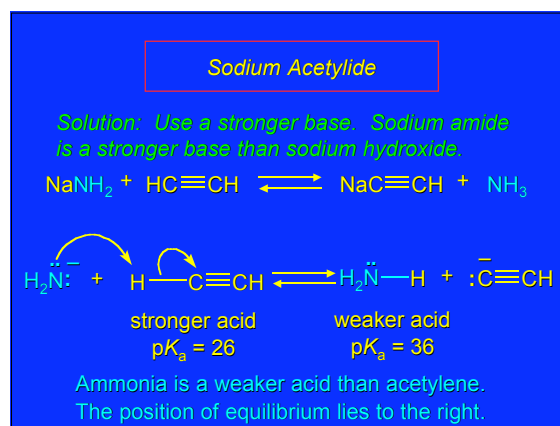
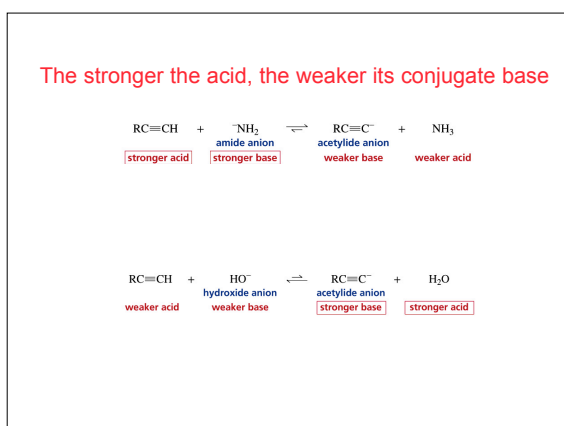
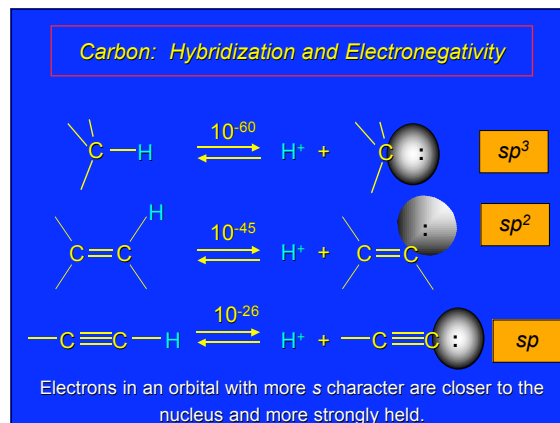
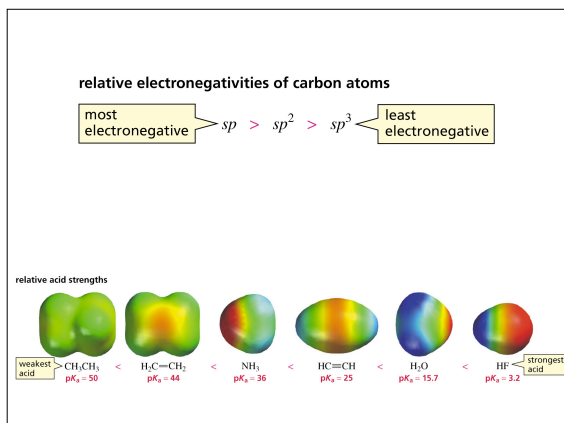
In general, hydrocarbons are exceedingly weak acids

Compound	pK_a
HF	3.2
H_2O	16
NH_3	36
$\text{H}_2\text{C}=\text{CH}_2$	45
CH_4	60

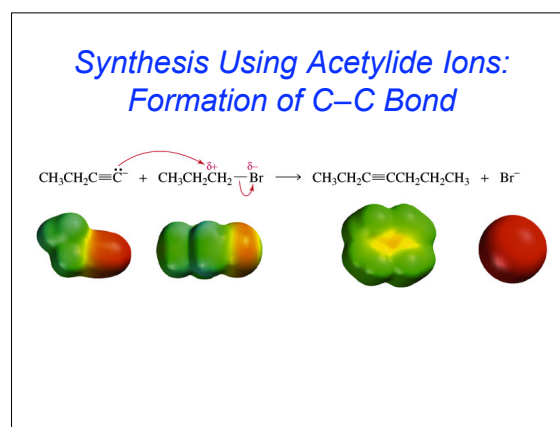
Acetylene

Acetylene is a weak acid, but not nearly as weak as alkanes or alkenes.

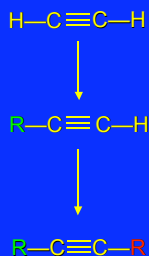
Compound	pK_a
HF	3.2
H_2O	16
$\text{HC}\equiv\text{CH}$	26
NH_3	36
$\text{H}_2\text{C}=\text{CH}_2$	45
CH_4	60



Preparation of Various Alkynes by alkylation reactions with Acetylide or Terminal Alkynes



Alkylation of Acetylene and Terminal Alkynes



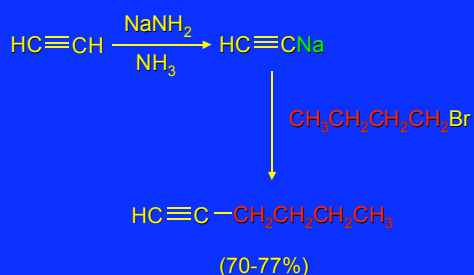
Alkylation of Acetylene and Terminal Alkynes



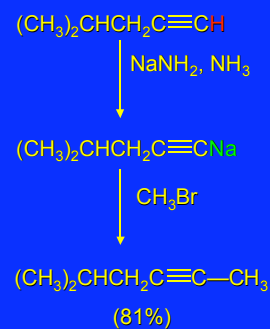
The alkylating agent is an alkyl halide, and the reaction is nucleophilic substitution.

The nucleophile is sodium acetylide or the sodium salt of a terminal (monosubstituted) alkyne.

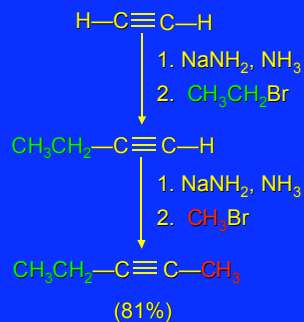
Example: Alkylation of Acetylene



Example: Alkylation of a Terminal Alkyne



Example: Dialkylation of Acetylene



Limitation

Effective only with primary alkyl halides

Secondary and tertiary alkyl halides undergo elimination

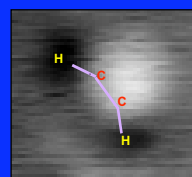
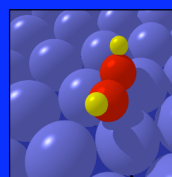
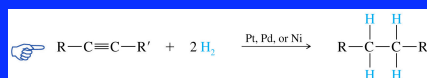
Reactions of Alkynes

Reactions of Alkynes

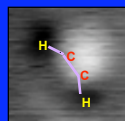
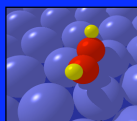
- ✓ Acidity
- Hydrogenation
- Metal-Ammonia Reduction
- Addition of Hydrogen Halides
- Addition of Halogens
- Hydration

Hydrogenation of Alkynes

Atomic Force Microscopy of Acetylene Lawrence Berkeley Laboratory (LBL)

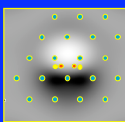
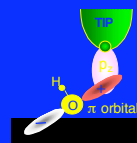


Imaging: acetylene on Pd(111) at 28 K



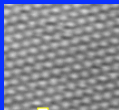
Molecular image
Tip scanning altitude ~700 pm
 $\lambda = 50 \text{ pm}$

Why don't we see the Pd atoms?
Because the tip needs to be very close to image the Pd atoms and would knock the molecule away



Calculated image
(Philippe Sautet)

Surface atomic profile
Tip scanning altitude ~900 pm
 $\lambda = 5 \text{ pm}$



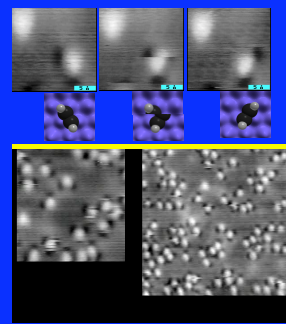
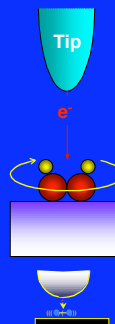
If the tip were made as big as an airplane, it would be flying at 1 cm from the surface and waving its arm down by 1 micrometer



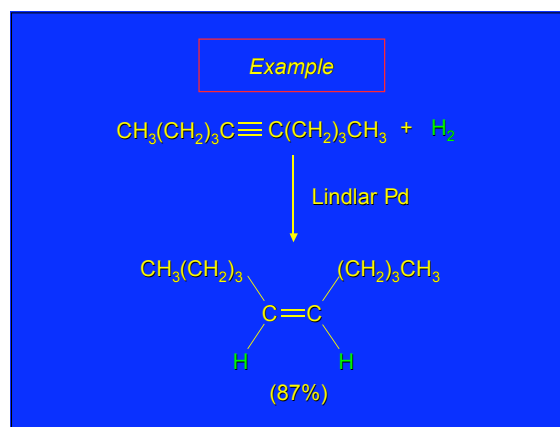
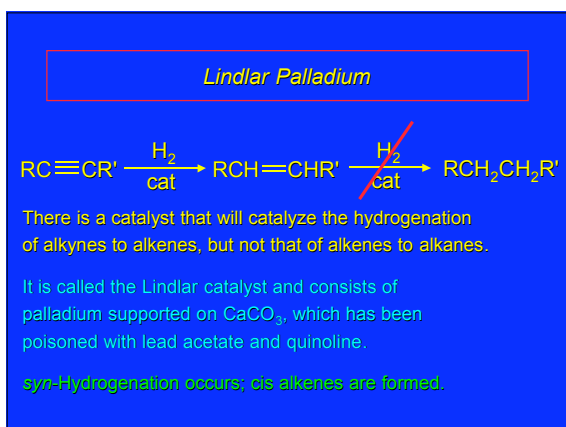
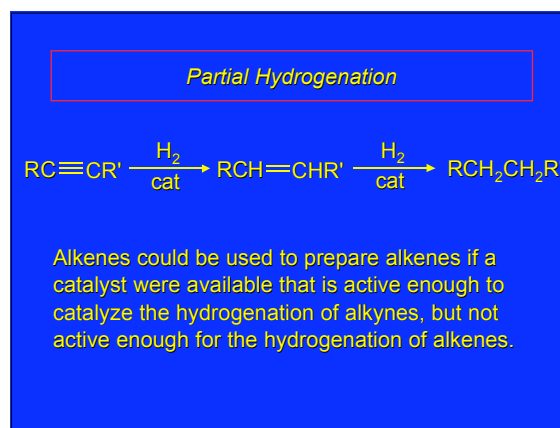
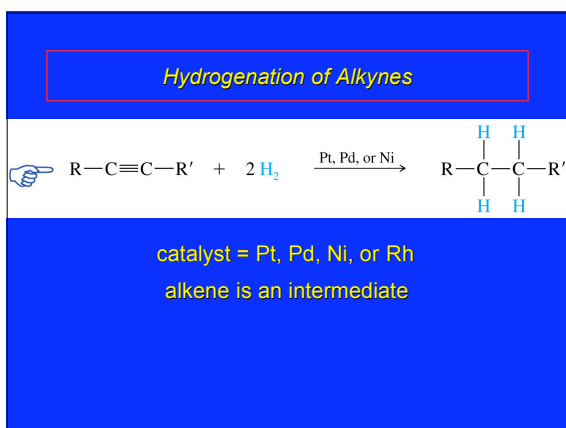
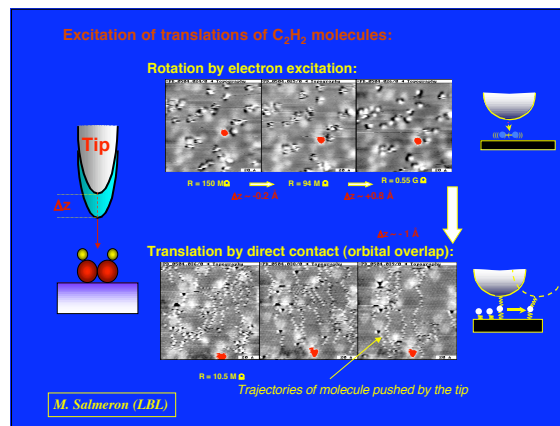
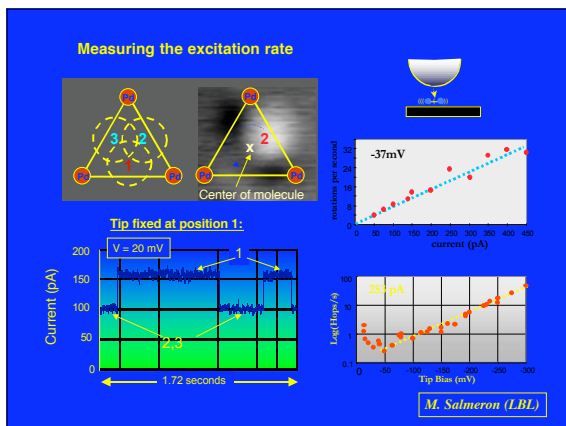
The STM image is a map of the pi-orbital of distorted acetylene

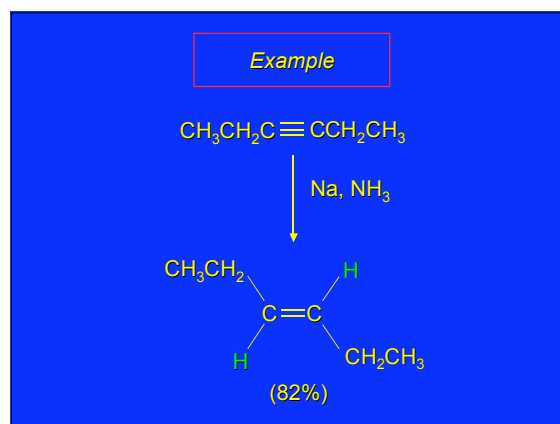
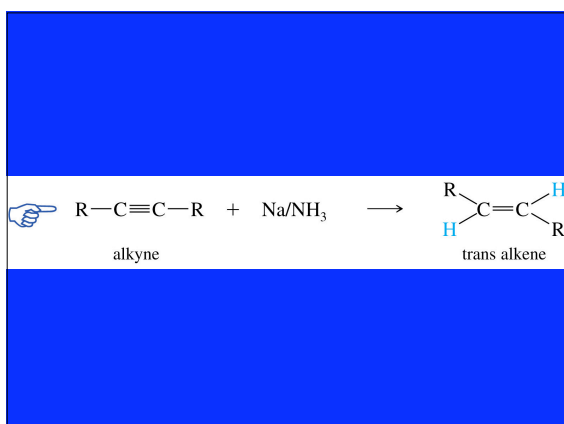
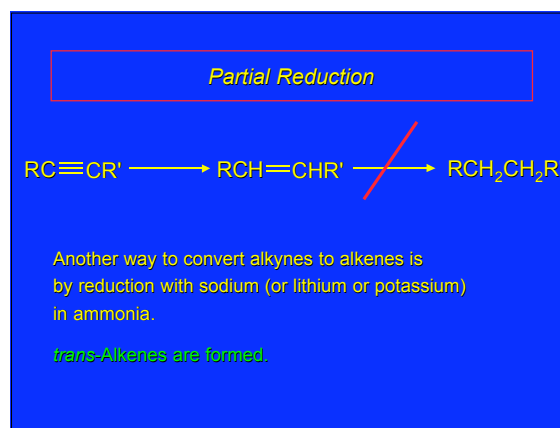
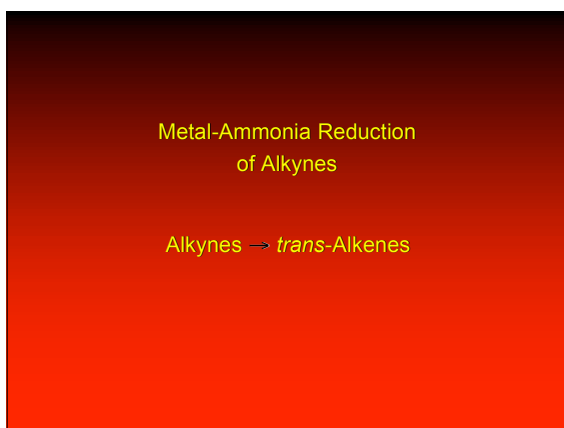
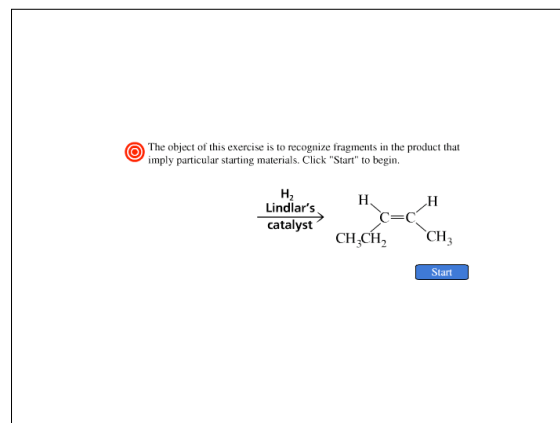
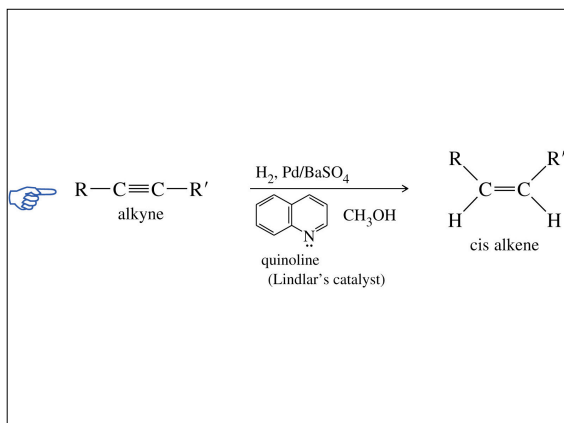
M. Salmeron (LBL)

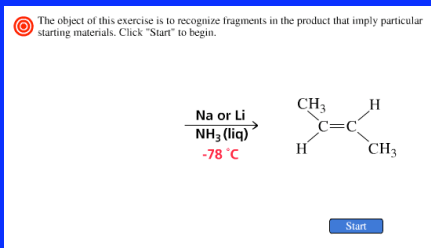
Excitation of frustrated rotational modes in acetylene molecules on Pd(111) at T = 30 K



M. Salmeron (LBL)





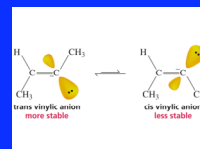


Mechanism

Metal (Li, Na, K) is reducing agent;
H₂ is not involved; proton comes from NH₃

four steps

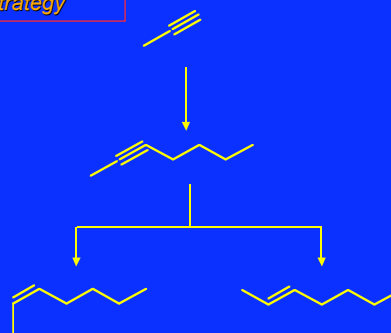
- (1) electron transfer
- (2) proton transfer
- (3) electron transfer
- (4) proton transfer



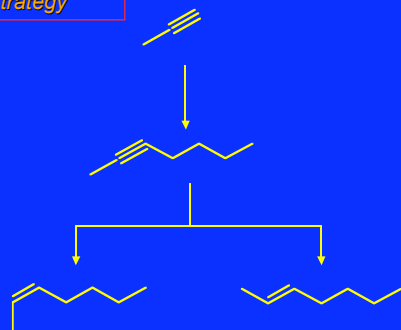
Problem

Suggest an efficient synthesis of (E)- and (Z)-2-heptene from propyne and any necessary organic or inorganic reagents.

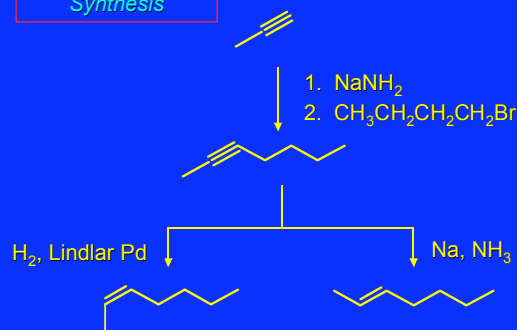
Problem Strategy



Problem Strategy

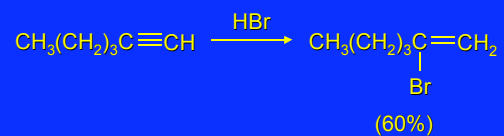


Problem Synthesis



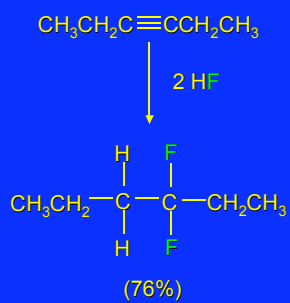
Addition of Hydrogen Halides
to Alkynes

Follows Markovnikov's Rule

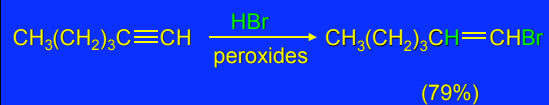


Alkynes are slightly less reactive than alkenes

Two Molar Equivalents of Hydrogen Halide



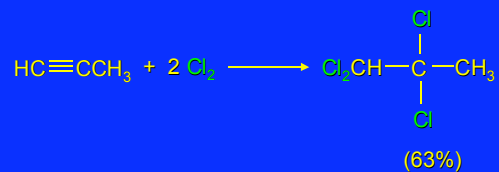
Free-radical Addition of HBr



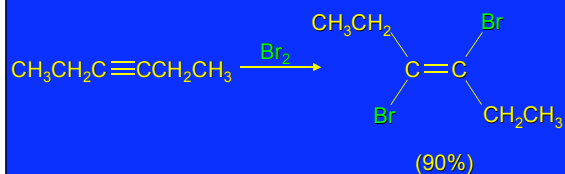
regioselectivity opposite to Markovnikov's rule

Addition of Halogens to Alkynes

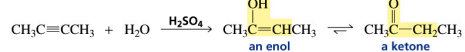
Example



Addition is anti

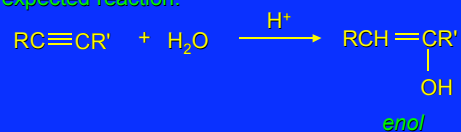


Hydration of Alkynes

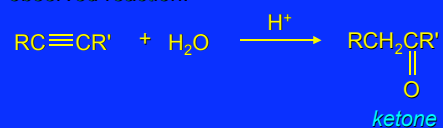


Hydration of Alkynes

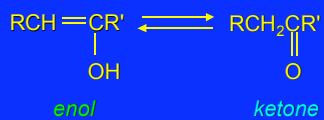
expected reaction:



observed reaction:



Enols

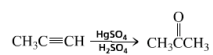


enols are regioisomers of ketones, and exist in equilibrium with them

keto-enol equilibration is rapid in acidic media

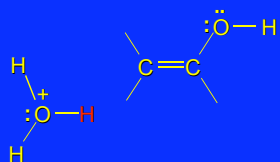
ketones are more stable than enols and predominate at equilibrium

Click "Start" to learn about each step in the mechanism.

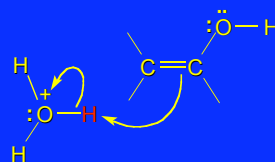


Start

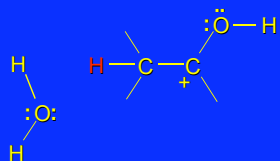
Mechanism of conversion of enol to ketone



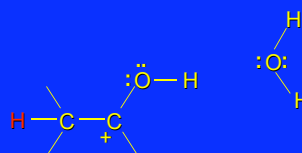
Mechanism of conversion of enol to ketone



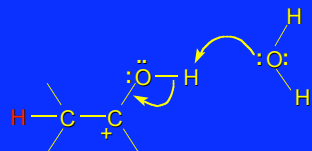
Mechanism of conversion of enol to ketone



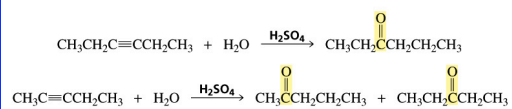
Mechanism of conversion of enol to ketone



Mechanism of conversion of enol to ketone



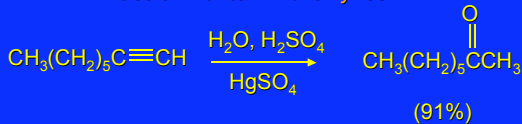
Useful for symmetrical starting alkynes to produce a single product.



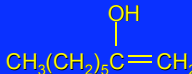
Unsymmetrical starting alkynes that are not terminal produce a mixture of ketones...non-regioselectively.

Regioselectivity

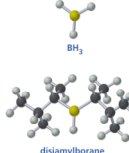
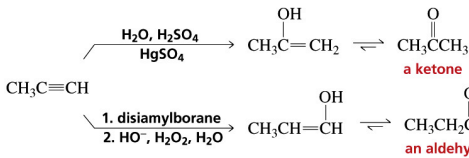
*Markovnikov's rule followed in formation of enol,
Useful with terminal alkynes.*



via



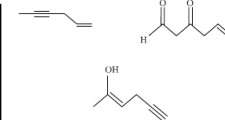
Aldehyde vs. Ketone



Can you identify and name the function?

 Touch a label on the left to see the corresponding atoms, or touch the atoms to see the appropriate label.

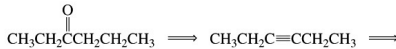
- aldehyde
- allyl group
- carbonyl group
- enol
- internal alkyne
- ketone
- terminal alkyne



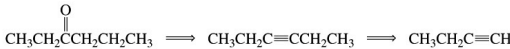
retrosynthetic analysis



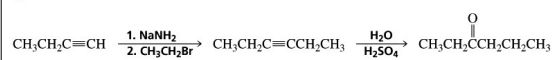
retrosynthetic analysis



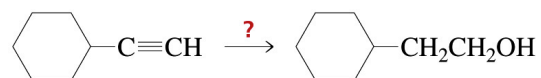
retrosynthetic analysis



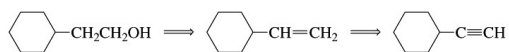
synthesis



Example



retrosynthetic analysis



synthesis

